

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Clarke et al

Parent Application

Serial No. Not Yet Known

Group Art Unit: 1772

Filing Date: Herewith

Examiner: Dye, R.L.

Title: Gas-permeable Membrane

Continuation of Serial No.: 08/759,602 filed December 5, 1996

Assistant Commissioner for Patents

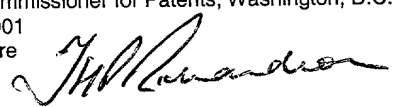
Washington, DC 20231

Version of Amended Claims with Markings to show Changes requested by the  
accompanying Preliminary Amendment, in accordance with 37 CFR 1.121(c)(1)(ii)

This paper sets out a version of each of the claims rewritten as requested by the accompanying Amendment under 37 CFR 1.312 (but not the claims which were unchanged or the claims which were added), marked up to show all the changes relative to the previous version of the claim. In this version,

- (i) a parenthetical expression (which is the same as the parenthetical expression in the clean version of claims set out in the Preliminary Amendment) follows the claim number and indicates the status of the claim as amended, and
- (ii) the changes are shown by brackets (for deleted matter) and underlining (for added matter).

**EXPRESS MAIL CERTIFICATION UNDER 37 CFR 1.10**

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1. (Amended) A gas-permeable membrane which is useful in the packaging of respiring biological materials and which comprises

(a) a microporous polymeric film comprising a network of interconnected pores such that gases can pass through the film, and

(b) a polymeric coating on the microporous film,

wherein

(1) the pores in the microporous film have an average pore size of less than 0.24 micron; and

(2) the microporous film was prepared by a process comprising the steps of

(A) preparing a uniform mixture comprising the polymeric matrix material in the form of a powder, the filler, and a processing oil;

(B) extruding the mixture as a continuous sheet;

(C) forwarding the continuous sheet, without drawing, to a pair of heated calender rolls;

(D) passing the continuous sheet through the calender rolls to form a sheet of lesser thickness;

(E) passing the sheet from step (D) to a first extraction zone in which to the processing oil is substantially removed by extraction with an organic extraction liquid which is a good solvent for the processing oil, a poor solvent for the polymeric matrix material, and more volatile than the processing oil;

(F) passing the sheet from step (E) to a second extraction zone in which the organic extraction liquid is substantially removed by steam or water or both; and

(G) passing the sheet from step (F) through a forced air dryer to remove residual water and organic extraction liquid; and

(3) the polymeric coating has a thickness such [the polymeric coating changing the permeability of the microporous film so] that the membrane

(i) has a  $P_{10}$  ratio, over at least one 10°C range between -5 and 15°C, of at least 1.3;

- (ii) has an oxygen permeability (OTR), at all temperatures between 20° and 25°C, of at least 775,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 cc/100 inch<sup>2</sup>.atm.24 hrs; and
  - (iii) has a CO<sub>2</sub>/O<sub>2</sub> permeability ratio(R) of at least 1.5;
- the P<sub>10</sub>, OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi)

2. A membrane according to claim 1 wherein [ which has at least one of the following characteristics

- (1) the microporous film has an average pore size of less than 0.24 micron;
- (2) the microporous film has a tear strength of at least 30g;
- (3) the microporous film has a Sheffield Smoothness of at least 30;
- (4)]

the microporous film comprises a polymeric matrix selected from the group consisting of [comprising]

- (i) an essentially linear ultrahigh molecular weight polyethylene having an intrinsic [intrinisc] viscosity of at least 18 deciliters/g and [;
- (5) the microporous film comprises a polymeric matrix comprising]
- (ii) an essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/g.];
- (6) the microporous film comprises a finely divided, particulate, substantially insoluble filler which is distributed throughout the film;
- (7) the coating weight of the coating polymer is 1.7 to 2.9 g/m<sup>2</sup>; and
- (8) the coating polymer is a crystalline polymer having a T<sub>p</sub> of -5° to 15°C.]

3. (Amended) A membrane according to claim 1 wherein at least 70% of the pores in the microporous film have a pore size of less than 0.24 micron. [ which has a P<sub>10</sub> ratio between 0 and 10°C of at least 2.6, the P<sub>10</sub> being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).]

4. (Amended) A membrane according to claim 1 wherein at least 90% of the pores in the microporous film have a pore size of less than 0.24 micron. [2 which has a  $P_{10}$  ratio between 0 and 10°C of at least 2.6, the  $P_{10}$  being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).]

5. (Amended) A membrane according to claim 1 wherein substantially 100% of the falls in the microporous film have a pore size of less than 0.24 micron. [ which has [a  $P_{10}$  ratio, over at least one 10°C range between -5°C and 15°C, of at least 2.6, an OTR at all temperatures between 20°C and 25°C of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/inch<sup>2</sup>.atm.24 hrs, and an R ratio of at least 2.5, the  $P_{10}$ , OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

[5.] 6. (Amended) A membrane according to claim [2 ] 1 wherein at least 80% of the pores in the microporous film have a pore size less than 0.15 micron and at least 70% of the pores have a pore size less than 0.11 micron. [which has a  $P_{10}$  ratio, over at least one 10°C range between -5°C and 15°C, of at least 2.6, an OTR at all temperatures between 20°C and 25°C of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/inch<sup>2</sup>.atm.24 hrs, and an R ratio of at least 2.5, the  $P_{10}$ , OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).]

7. (Amended) A membrane according to claim 1 [wherein at least 90% of the pores have a pore size less than 0.24 micron, and] which has [a  $P_{10}$  ratio, over at least one 10°C range between -5 and 15°C of at least 1.3,] an OTR of at least 1,550,000 [775,000 to 3,100,000] ml/m<sup>2</sup> atm.24 hrs ( 100,000 [50,000 to 200,000] cc/100 inch<sup>2</sup>.atm 24 hrs), and an R ratio of at least 2, the [ $P_{10}$ , ]OTR and R values being measured at a pressure of 0.7 kg/cm<sup>2</sup> (10 psi).

8. (Amended) A membrane according to claim 7 which has [at least one of the following characteristics

- (1) it has a  $P_{10}$  ratio of at least 1.3 over at least one 10°C temperature range between 0° and 15°C;

- (2) it has a  $P_{10}$  ratio of at least 2 over at least one  $10^{\circ}\text{C}$  temperature range between  $0^{\circ}$  and  $15^{\circ}\text{C}$ ;
- (3) it has a  $P_{10}$  ratio of at least 2.5 over at least one  $10^{\circ}\text{C}$  temperature range between  $0^{\circ}$  and  $15^{\circ}\text{C}$ ;
- (4) it has an OTR of at least  $1,550,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $100,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ );
- (5) it has] an OTR of at least  $2,325,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $150,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ ),[;
- (6) it has an OTR of  $775,000$  to  $3,100,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $50,000$  to  $200,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ ) and an R value of more than  $(3.8 - 0.00000045P)$ , where P is the OTR in  $\text{ml/m}^2.\text{atm.24 hrs}$ ;
- (7) it has an OTR of  $775,000$  to  $3,100,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $50,000$  to  $200,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ ) and an R value of  $(3.8 - 0.0000045P)$  to  $(7.4 - 0.000016P)$ , where P is the OTR in  $\text{ml/m}^2.\text{atm.24 hrs}$ ;
- (8) it has an OTR of  $775,000$  to  $3,100,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $50,000$  to  $200,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ ) and an R value of  $(3.8 - 0.0000045P)$  to  $(5.6 - 0.000084P)$ , where P is the OTR in  $\text{ml/m}^2.\text{atm.24 hrs}$ ;
- (9) it has an R ratio of at least 2.5; and
- (10) it has an R ratio of at least 3.

the  $P_{10}$ , OTR and R values being ] measured at a pressure of  $0.07 \text{ kg/cm}^2$  (10 psi).

Claims 9 and 10 canceled

11. (Amended) A membrane according to claim 1 [ 7] wherein the coating polymer [has at least one of the following characteristics:

- (1) it is a crystalline polymer having a  $T_p$  of  $-5$  to  $40^{\circ}\text{C}$  and a  $\Delta H$  of at least  $5 \text{ J/g}$ ;
- (2) it is a crystalline polymer having a  $T_p$  of  $0$  to  $15^{\circ}\text{C}$  and a  $\Delta H$  of at least  $20 \text{ J/g}$ ;
- (3) it is a side chain crystalline polymer;

- (4) it is a side chain crystalline polymer in which  $T_p - T_o$  is less than  $10^\circ\text{C}$ ;
- (5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;
- (6) it] is [cis-polybutadiene, poly(4-methylpentene), ]polydimethyl siloxane [, or ethylene-propylene rubber; and
- (7) it has been crosslinked].

12. (Amended) A membrane according to claim 1 [8] wherein the coating polymer [has at least one of the following characteristics:

- (1) it is a crystalline polymer having a  $T_p$  of  $-5$  to  $40^\circ\text{C}$  and a  $\Delta H$  of at least 5 J/g;
- (2) it is a crystalline polymer having a  $T_p$  of  $0$  to  $15^\circ\text{C}$  and a  $\Delta H$  of at least 20 J/g;
- (3) it is a side chain crystalline polymer;
- (4) it is a side chain crystalline polymer in which  $T_p - T_o$  is less than  $10^\circ\text{C}$ ;
- (5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;
- (6) it] is cis-polybutadiene, poly(4-methylpentene)[, polydimethyl siloxane,] or ethylene-propylene rubber[; and
- (7) it has been crosslinked].

13. (Amended) A membrane according to claim 1 [9] wherein the coating polymer [has at least one of the following characteristics:

- (1) it is a crystalline polymer having a  $T_p$  of  $-5$  to  $40^\circ\text{C}$  and a  $\Delta H$  of at least 5 J/g;

- (2) it is a crystalline polymer having a  $T_p$  of 0 to 15°C and a  $\Delta H$  of at least 20 J/g;
- (3) it is a side chain crystalline polymer;
- (4) it is a side chain crystalline polymer in which  $T_p - T_o$  is less than 10°C;
- (5) it is a side chain crystalline polymer prepared by copolymerizing (i) at least one n-alkyl acrylate or methacrylate in which the n-alkyl group contains at least 12 carbon atoms and (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms;
- (6) it is cis-polybutadiene, poly(4-methylpentene), polydimethyl siloxane, or ethylene-propylene rubber; and
- (7) it] has been crosslinked.

14. (Unchanged)

15. (Unchanged)

16. (Amended) A package which is stored in air and which comprises

- (a) a sealed container, and
- (b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material,

the sealed container including one or more permeable control sections which provide at least the principal pathway [substantially the only pathways] for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as defined in claim 1.

Claims 17-19 canceled

Respectfully submitted,

  
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Continuation of Serial No.: 08/759,602 filed December 5, 1996

Assistant Commissioner for Patents  
Washington, DC 20231

PRELIMINARY AMENDMENT

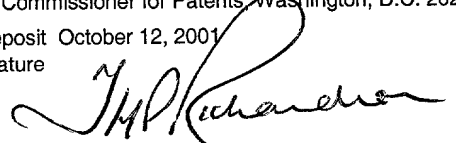
Sir,

Before examining this application, and before calculating the filing fee, please amend this application has set out below. The Remarks section at the end of this Preliminary Amendment provides comments on the amendments which the Examiner may wish to read before considering the amendments themselves.

EXPRESS MAIL CERTIFICATION UNDER 37 CFR 1.10

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Typed name of person signing this certificate: T. H. P. Richardson Signature



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In the Specification

1. Please rewrite the paragraph beginning on page 1, line 3 (with the words "This application...") and ending on page 1, line 8 (with the words "... as inventors.") as follows.

-- This application is a continuation of copending application Serial No. 08/759,602, filed December 5, 1996, by Raymond Clarke, Ray Stewart, Valentine Yoon, Donald Schultz and Bradley McClary. Serial No. 08/759,602 is a continuation-in-part of application Serial No. 08/453,108, filed May 30, 1995, by Raymond Clarke, Ray Stewart, Valentine Yoon, Donald Schultz and Bradley McClary, now abandoned. This application is also related to and claims priority under 35 U.S.C. 119 and 365 from International Application number PCT/U.S. 96/07939, filed May 29, 1996, by Landec Corp., naming Raymond Clarke, Ray Stewart, Valentine Yoon, Donald Schultz and Bradley McClary as inventors. The entire disclosure of each of Serial numbers 08/453,108 and 08/759,602 and PCT/U.S. 96/0939 is incorporated herein by reference for all purposes. --

2. Please rewrite the paragraph beginning on page 2, line 27 (with the words "In describing...") and ending on page 3, line 15 (with the words "... second heating cycle.") as follows.

-- In describing the invention below, the following abbreviations, definitions, and methods of measurement are used. OTR is  $O_2$  permeability. COTR is  $CO_2$  permeability. OTR and COTR values are given in  $ml/m^2 \cdot atm \cdot 24 \text{ hrs}$ , with the equivalent in  $cc/100 \text{ inch}^2 \cdot atm \cdot 24 \text{ hrs}$  given in parentheses. OTR and COTR were measured using a permeability cell (supplied by Millipore) in which a mixture of  $O_2$ ,  $CO_2$  and helium is applied to the sample, using a pressure of  $0.7 \text{ kg/cm}^2$  (10 psi) except where otherwise noted, and the gases passing through the sample were analyzed for  $O_2$  and  $CO_2$  by a gas chromatograph. The cell could be placed in a water bath to control the temperature. The abbreviation  $P_{10}$  is used to denote the ratio of the oxygen

permeability at a first temperature  $T_1^\circ\text{C}$  to the oxygen permeability at a second temperature  $T_2$ , where  $T_2$  is  $(T_1-10)^\circ\text{C}$ ,  $T_1$  being  $10^\circ\text{C}$  and  $T_2$  being  $0^\circ\text{C}$  unless otherwise noted. The abbreviation  $R$  is used to denote the ratio of  $\text{CO}_2$  permeability to  $\text{O}_2$  permeability, both permeabilities being measured at  $20^\circ\text{C}$  unless otherwise noted. Pore sizes given in this specification are measured by mercury porosimetry or an equivalent procedure. Parts and percentages are by weight, temperatures are in degrees Centigrade, and molecular weights are weight average molecular weights expressed in Daltons. For crystalline polymers, the abbreviation  $T_o$  is used to denote the onset of melting, the abbreviation  $T_p$  is used to denote the crystalline melting point, and the abbreviation  $\Delta H$  is used to denote the heat of fusion.  $T_o$ ,  $T_p$  and  $\Delta H$  are measured by means of a differential scanning calorimeter (DSC) at a rate of  $10^\circ\text{C}/\text{minute}$  and on the second heating cycle.  $T_o$  and  $T_p$  are measured in the conventional way well known to those skilled in the art. Thus  $T_p$  is the temperature at the peak of the DSC curve, and  $T_o$  is the temperature at the intersection of the baseline of the DSC peak and the onset line, the onset line being defined as the tangent to the steepest part of the DSC curve below  $T_p$ . --

3. Please rewrite the paragraph beginning on page 5, line 1 (with the words "In the coating...") and ending on page 5, line 13 (with the words "... biological material.") as follows.

-- The coating polymer should be selected so that the membrane has a desired  $P_{10}$  ratio and a desired  $R$  ratio, and should be coated onto the microporous film at a coating weight which results in a membrane having the desired balance between the permeability characteristics of the microporous film and of the coating polymer. For example, by choosing a crystalline coating polymer whose  $T_p$  is within or a little below an expected range of storage temperatures, it is possible to produce a membrane whose  $P_{10}$  is relatively large in the storage temperature range; furthermore, the size of the  $P_{10}$  ratio can be increased by increasing the  $\Delta H$  of the coating polymer. Similarly, a membrane having a relatively large (or small)  $R$  ratio can be produced by selecting a coating polymer having a relatively high (or small) inherent  $R$  ratio. In this way, the

invention makes it possible to produce membranes whose properties can be tailored, much more closely than was previously possible, to the needs of a particular respiring biological material. --

4. Please rewrite the paragraph beginning on page 5, line 28 (with the words "in a second preferred aspect, this invention...") and ending on page 6, line 6 (with the words "... as defined in the first aspect of the invention. ") by the following paragraph.

-- In a second preferred aspect, this invention provides a package which is stored in air and which comprises

- (a) a sealed container, and
- (b) within the sealed container, a respiring biological material and packaging atmosphere around the biological material;

the sealed container including one or more permeable control sections which provide at least the principal pathway, and optionally substantially the only pathway, for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as defined in the first aspect of the invention. --

5. Please rewrite the paragraph beginning on page 7, line 24 (with the words "the preferred...") and ending on page 8, line 5 (with the words "... tradename 'Teslin'.") as follows.

-- The preferred base film includes a finely divided, particulate, substantially water-insoluble, inorganic filler, for example a siliceous filler, which is distributed throughout the matrix and which is present in amount 50 to 90%, particularly 50 to 85%, by weight of the base film. The filler is preferably silica, particularly precipitated silica, especially silica having an average ultimate particle size of less than 0.1 micrometer. Preferably the filler occupies 35 to 80% of the total volume of microporous film. Particularly preferred, because they have a relatively narrow range of pore sizes, are films made a process comprising the steps of

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- (A) preparing a uniform mixture comprising the polymeric matrix material in the form of a powder, the filler, and a processing oil;
- (B) extruding the mixture as a continuous sheet;
- (C) forwarding the continuous sheet, without drawing, to a pair of heated calender rolls;
- (D) passing the continuous sheet through the calender rolls to form a sheet of lesser thickness;
- (E) passing the sheet from step (D) to a first extraction zone in which the processing oil is substantially removed by extraction with an organic extraction liquid which is a good solvent for the processing oil, a poor solvent for the polymeric matrix material, and more volatile than the processing oil;
- (F) passing the sheet from step (E) to a second extraction zone in which the organic extraction liquid is substantially removed by steam or water or both; and
- (G) passing the sheet from step (F) through a forced air dryer to remove residual water and organic extraction liquid.

Such films are disclosed in US Patent Nos. 4,937,115 and 3,351,495, the disclosures of which are incorporated herein by reference, and are sold by PPG Industries under the tradename "Teslin". --

6. Please replace the paragraph beginning on page 15, line 7 (with the words "SCC 1-15...") and ending on page 15, line 22 (with the word "... respectively.") as follows.

-- SCC 1-15 and ACP. These acrylate polymers were prepared by polymerizing the monomers and parts by weight thereof shown in Table 1. In Table 1, the following abbreviations are used for the monomers. AA is acrylic acid, MAA is methacrylic acid, EHA is 2-ethylhexyl acrylate, C4A is butyl acrylate, C6A is hexyl acrylate, CY6MA is cyclohexylmethacrylate, C6DA is hexyldiacrylate, C12A is dodecyl acrylate, C12DA is dodecyl diacrylate, C14A is tetradecyl acrylate, C16A is hexadecyl acrylate, and C22A

is behenyl acrylate. The monomers were copolymerized in a suitable solvent, e.g. toluene or a mixture of heptane and butyl acetate or ethyl acetate, using a suitable initiator, e.g. azobisisobutyronitrile (AIBN). For example, SCC11 was made by mixing the C6A and C14A with 0.31 parts of AIBN in a 4:1 mixture of heptane and ethyl acetate, and maintaining the mixture at 50°C for 2 days, to give a product having a weight average molecular weight of about 970,000 and a  $T_p$  of about 12.5°C. SCC 5 was made by polymerizing the C22A alone, functionalizing the resulting homopolymer with isocyanatoethylmethyl methacrylate, and then polymerizing the other monomers with the functionalized homopolymer. --

7. Please rewrite the paragraph beginning on page 18, line 10 (with the words "Examples 1-10...") and ending on page 18, line 16 (with the word "... ratios.") as follows.

-- Examples 1-10 and C1-4 are summarized in Tables 2-4 below. In each of the tests, the substrate identified in Table 2 was coated with a solution containing the identified percentage of the identified coating polymer. The coated substrate was dried, and its permeability to  $O_2$  and  $CO_2$  was measured at the temperature indicated in Table 2. The results are reported in Table 2. In some cases, the  $P_{10}$  ratios were calculated, as shown in Tables 3 and 4. --

8. Please replace Table 2 on page 19 with the following amended Table 2.

T.D.T. 48694650

Table 2

Ex No.	Substrate	Coating Polymer		Permeability		
		Type	%	OTR	Ratio CO <sub>2</sub> /O <sub>2</sub>	°C
*1A	CG	SCC1	2	**	1.0	20
*B			5	**	1.0	20
*C			10	**	1.0	20
*D			20	**	1.0	20
*E	MSX	SCC1	2	**	1.0	20
*F			5	**	1.0	20
*G			10	**	1.0	20
*H			20	487,475 (31,450)	1.86	20
*I			25	63,689 (4,109)	5.75	20
*J			30	44,175 (2,850)	6.5	20
*K	Van L	SCC1	2	403,077 (26,005)	1.32	20
*L			5	29,636 (1,912)	3.92	20
*M			10	62,558 (4,036)	2.39	20
*N			20	62,310 (4,020)	2.42	20
O	Teslin SP7	SCC1	2	2,413,458 (155,707)	2.95	20
P			5	1,021,140 (65,880)	4.86	20
Q			10	602,547 (38,874)	5.22	20
R			20	425,025 (27,421)	5.48	20
2A	Teslin SP7	Tflex	5	1,076,537 (69,454)	2.34	20
*B			7	238,024 (15,368)	5.9	20
*C			15	108,856 (7,023)	6.19	20
D	Teslin SP7	Sil	35	1,607,799 (103,729)	2.98	20
E			40	987,319 (63,698)	4.13	20
F			50	809,627 (52,234)	4.7	20
*G			100	391,824 (25,279)	5.3	20
H	Teslin SP7	CisPB	2	3,712,994 (239,548)	2.8	20
I			5	2,451,728 (158,176)	4.39	20
J			10	888,987 (57,354)	6.45	20
*K			20	392,925 (25,350)	7.2	20
*L	Teslin SP7	Kton	5	293,570 (18,940)	4.4	20
*M			10	116,606 (7,523)	4.7	20
*N			20	46,887 (3,025)	5.0	20
O	Teslin SP7	TPX	5	974,841 (62,893)	3.35	20
P			5	923,598 (59,587)	3.3	20
Q			2	2,798,478 (180,547)	2.38	20

\*comparative example

\*\*permeability too high to measure

9. Please replace Table 2 (continued) on page 19 with the following amended Table 2 (continued).

Table 2 (continued)

Ex. No.	Substrate	Coating Polymer		Permeability		
		Type	%	OTR	Ratio CO <sub>2</sub> /O <sub>2</sub>	°C
3A	Teslin SP7	SCC2	10	637,592 (41,135)	4.94	20
B		SCC3	5	927,861 (59,862)	4.81	20
*C		ACP	5	403,728 (26,047)	5.8	20
D		CisPB	5	2,092,934 (135,028)	4.8	20
E		*CisPB + SCC8	5	1,205,559 (77,778)	5.3	20
F		SCC4	2	1,883,389 (121,509)	3.3	20
*G		SCC4	10	687,688 (44,367)	5.2	20
H		SCC5	-	930,854 (60,055)	4.72	20
I		SCC6	10	812,959 (52,449)	5.10	20
*J		SCC7	25	410,440 (26,480)	5.23	20
4A	Teslin SP7	CisPB	5	125,218 (80,786)	6.50	0
B		CisPB	5	1,367,875 (88,250)	6.09	5
C		CisPB	5	1,579,000 (101,871)	5.51	10
D		CisPB	5	1,839,323 (118,666)	5.43	15
E		CisPB	5	2,092,934 (135,028)	4.82	20
F		CisPB	5	2,328,952 (150,255)	4.55	25
*G		*CisPB + SCC8	5	320,617 (20,685)	5.5	0
*H		*CisPB + SCC8	5	394,304 (25,439)	5.5	5
*I		*CisPB + SCC8	5	512,848 (33,087)	5.4	10
*J		*CisPB + SCC8	5	722,455 (46,610)	5.3	15
K		*CisPB + SCC8	5	1,205,559 (77,778)	5.3	20
L		*CisPB + SCC8	5	1,520,379 (98,089)	5.2	25
M		SCC10	5	1,020,628 (65,847)	5.93	22.2

\*a mixture of CisPB (80 parts) and SCC8 (20 parts)

11. Please replace Table 2 (continued) on page 21 with the following amended Table 2 (continued)

Table 2 (continued)

Ex. No.	Substrate	Coating Polymer		Permeability		
		Type	%	OTR	Ratio CO <sub>2</sub> /O <sub>2</sub>	°C
*5A	Teslin SP7	SCC11	6.5	†386,461 (24,933)	6.06	0
*B			6.5	†521,141 (33,622)	6.16	5
C			6.5	†1,048,590 (67,651)	6.12	10
D			6.5	†1,474,933 (95,157)	5.78	15
E			6.5	†1,825,001 (117,742)	5.53	20
F			6.5	†2,225,753 (143,597)	5.21	25
G			6.5	†2,587,33 (166,926)	4.88	30
6	Teslin SP7	SCC12	6.5	†1,286,500 (83,000)	5.29	22
7A	Teslin X457	SCC13	2	†4,022,699 (259,529)	3.92	22
B			1.5	†8,789,414 (567,059)	2.62	22
C			1.3	†13160,662 (849,075)	1.68	22
7D	Teslin SP7	SCC13	1	†8,693,239 (560,854)	2.75	22
E			1.5	†3,262,486 (210,483)	4.88	22
F			2	†2,766,083 (178,547)	5.48	22
G			3	†1,869,005 (120,581)	6.03	22
8	Teslin SP7	SCC13	3	†1,518,643 (97,977)	6.32	22
9		SCC15	6.5	†1,758,196 (113,432)	5.58	22
10		SCC16	3.8	†1,113,241 (71,822)	7.06	22
*C1	Roplast	None	-	†3,859 (249)		22
*C2	BF915	None	-	†4,836 (312)		22
*C3	LB710	None	-	†5,161 (333)		22
*and C4	CVP	None	-	†5,130 (331)		22

† OTR and COTR were measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi) in Examples 5-10 and C1-C4.



12. Please replace Table 3 on page 21 with the following amended Table 3

Table 3

Ex No	3A	3B	3C*	3D	3E	3F	3G*	3H	3I	3J*
P <sub>10</sub> (0-10°C)	2.79	2.00	1.31	1.26	1.60	2.41	3.13	-	4.72	4.33
P <sub>10</sub> (20-30°C)	-	-	-	1.34	2.35	-	-	2.73	-	-

13. Please replace Table 4 on page 21 with the following amended Table 4

Table 4

Ex No	4A	*4G	5A	8	9	10	11	*C1	*C2	*C3	*C4
P <sub>10</sub> (0-10°C)	1.26	1.6	†2.7 1	†1. 4	†2. 4	†2.8	†3. 5	†1.5 4	†1.8 2	†1.7 4	†1.7 9
P <sub>10</sub> (10-20°C)	1.33	2.35	-	-	-	-	-	-	-	-	-

† OTR's in Examples 5A, 8-10 and C1-C4 were measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi).

14. Please rewrite the paragraph beginning on page 23, line 3 (beginning with the words "Example 13 is...") and ending on page 23, line 15 (with the words "... and 55 °C.") as follows.

-- Example 13 is summarized in Table 6. Fresh broccoli was sealed into storage bags (23 x 28 cm) and stored for 13 days at 45° F, or for 9 days at 45° F and 4 days at 55° F. Four control bags (C5 - C8) were composed entirely of polyethylene. The other four bags (13A - 13D) were bags of the invention and were identical to the control bags except that a hole of 4.76 cm diameter was cut in the polyethylene and sealed by means of a membrane which had an O<sub>2</sub> permeability of 1,224,500 (79,000) and which had been prepared by coating Teslin SP7 with the SCC10 polymer. At the end of the storage period, the O<sub>2</sub> and CO<sub>2</sub> concentrations in the bag were measured. The results are shown in Table 5. The broccoli was then cooked for 1 minute in a microwave oven at the "high" setting. The broccoli from all the control bags had a strong and offensive odor and flavor before and after cooking. The broccoli from all the bags of the invention

had no unpleasant odor or flavor before or after cooking; the broccoli stored at 45° F for all 13 days was in better condition than that stored at 45° F and 55° F. --

15. Please replace Table 6 on page 23 by the following amended Table 6.

Table 6

	Storage		After Storage	
	Days at 45° F	Days at 55°F	% CO <sub>2</sub>	% O <sub>2</sub>
C5	13	0	8.3	0.29
C6	13	0	8.0	0.79
C7	9	4	9.1	0.46
C8	9	4	8.5	0.32
13A	13	0	4.1	2.89
13B	13	0	4.8	10.9
13C	9	4	4.1	1.04
13D	9	4	4.3	1.00

16. Please rewrite the paragraph beginning on page 25, line 10 (beginning with the words "Sample 16B...") and ending on page 25, line 11 (with the words "... and pressure.") as follows.

-- Sample 16B A laminate of Sample 16 A and Teslin SP7, the Teslin being laminated to the coated face of Sample 16A under heat and pressure. --

#### In the Claims

Please rewrite claims 1-8, 11-13 and 16 as set out below; cancel claims 9, 10, and 17-19; and add new claims 20-29 set out below.

In accordance with 37 CFR 121 (c):

- (1) A clean version of the entire set of pending claims is set out below. In this version,
  - (i) the amended claims are without markings to indicate the changes made,

(ii) in each claim, a parenthetical expression follows the claim number indicating the status of the claim as amended, unchanged or view, and the cancellation of claims 9, 10, and 17-19 has been noted.

(2) Attached hereto is a separate paper entitled "Version of Amended Claims with Markings to show Changes requested by the Accompanying Preliminary Amendment, in accordance with 37 CFR 1.121(c)(1)(ii)". This separate paper sets out each of the rewritten claims, marked up to show all the changes relative to the previous version of the claim. In this version,

(i) a parenthetical expression (which is the same as the parenthetical expression in the clean version of claims set out below) follows the claim number and indicates the status of the claim as amended, and

(ii) the changes are shown by brackets (for deleted matter) and underlining (for added matter).

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1. (Amended) A gas-permeable membrane which is useful in the packaging of respiring biological materials and which comprises

- (a) a microporous polymeric film comprising a network of interconnected pores such that gases can pass through the film, and
- (b) a polymeric coating on the microporous film,

wherein

- (1) the pores in the microporous film have an average pore size of less than 0.24 micron; and
- (2) the microporous film was prepared by a process comprising the steps of
  - (A) preparing a uniform mixture comprising the polymeric matrix material in the form of a powder, the filler, and a processing oil;
  - (B) extruding the mixture as a continuous sheet;
  - (C) forwarding the continuous sheet, without drawing, to a pair of heated calender rolls;
  - (D) passing the continuous sheet through the calender rolls to form a sheet of lesser thickness;
  - (E) passing the sheet from step (D) to a first extraction zone in which to the processing oil is substantially removed by extraction with an organic extraction liquid which is a good solvent for the processing oil, a poor solvent for the polymeric matrix material, and more volatile than the processing oil;
  - (H) passing the sheet from step (E) to a second extraction zone in which the organic extraction liquid is substantially removed by steam or water or both; and
  - (I) passing the sheet from step (F) through a forced air dryer to remove residual water and organic extraction liquid; and
- (3) the polymeric coating has a thickness such that the membrane
  - (i) has a  $P_{10}$  ratio, over at least one  $10^{\circ}\text{C}$  range between  $-5$  and  $15^{\circ}\text{C}$ , of at least 1.3;
  - (ii) has an oxygen permeability (OTR), at all temperatures between  $20^{\circ}$

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and 25°C, of at least 775,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 cc/100 inch<sup>2</sup>.atm.24 hrs; and

(iii) has a CO<sub>2</sub>/O<sub>2</sub> permeability ratio(R) of at least 1.5;  
the P<sub>10</sub>, OTR and R values being measured at a pressure of 0.035 kg/cm<sup>2</sup> (0.5 psi)

2. (Amended) A membrane according to claim 1 wherein the microporous film comprises a polymeric matrix selected from the group consisting of

- (i) an essentially linear ultrahigh molecular weight polyethylene having an intrinsic viscosity of at least 18 deciliters/g and
- (ii) an essentially linear ultrahigh molecular weight polypropylene having an intrinsic viscosity of at least 6 deciliters/g.

3. (Amended) A membrane according to claim 1 wherein at least 70% of the pores in the microporous film have a pore size of less than 0.24 micron.

4. (Amended) A membrane according to claim 1 wherein at least 90% of the pores in the microporous film have a pore size of less than 0.24 micron.

5. (Amended) A membrane according to claim 1 wherein substantially 100% of the pores in the microporous film have a pore size of less than 0.24 micron.

6. (Amended) A membrane according to claim 1 wherein at least 80% of the pores in the microporous film have a pore size less than 0.15 micron and at least 70% of the pores have a pore size less than 0.11 micron.

7. (Amended) A membrane according to Claim 1 which has an OTR of at least 1,550,000 ml/m<sup>2</sup>.atm.24 hrs (100,000 cc/inch<sup>2</sup>.atm.24 hrs), and an R ratio of at least 2, the OTR and R values being measured at a pressure of 0.7 kg/cm<sup>2</sup> (10 psi).

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1.00 10.00 10.00

8. (Amended) A membrane according to claim 7 which has an OTR of at least 2,325,000 ml/m<sup>2</sup>.atm.24 hrs (150,000 cc/100 inch<sup>2</sup>.atm.24 hrs) measured at a pressure of 0.7 kg/cm<sup>2</sup> (10 psi).

Claims 9 and 10 canceled by this Preliminary Amendment.

11. (Amended) A membrane according to claim 1 wherein the coating polymer is polydimethyl siloxane.

12. (Amended) A membrane according to claim 1 wherein the coating polymer is cis-polybutadiene, poly(4-methylpentene) or ethylene-propylene rubber.

13. (Amended) A membrane according to claim 1 wherein the coating polymer has been crosslinked.

14. (Unchanged) A membrane according to claim 1 wherein the coating polymer has at least one of the following characteristics:

- (1) it is an acrylate polymer containing at least 40% by weight of units derived from a cycloalkyl acrylate or methacrylate;
- (2) it is a fluoropolymer;
- (2) it is an acrylate polymer containing units derived from a fluoroalkyl acrylate or methacrylate;
- (3) it is an acrylate polymer containing 10 to 70% of units derived from a polyethylene glycol acrylate or methacrylate.

15. (Unchanged) A membrane according to claim 1 wherein the microporous polymeric film contains pores which are partially blocked by a polymer having an R ratio of less than 1.3 or by a particulate material, or (b) has an OTR before coating of less than 15,500,000 (1,000,000).

16. (Amended) A package which is stored in air and which comprises

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- (a) a sealed container, and
- (b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material;

the sealed container including one or more permeable control sections which provide at least the principal pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as defined in claim 1.

Claims 17-19 canceled by this Preliminary Amendment

20. (New) A gas-permeable membrane which is useful in the packaging of respiring biological materials and which comprises

- (a) a microporous polymeric film comprising a network of interconnected pores such that gases can pass through the film, and
- (b) a polymeric coating on the microporous film,

wherein

- (1) the pores in the microporous film have an average pore size of less than 0.24 micron;
- (2) at least 70% of the pores in the microporous film have a pore size of less than 0.24 micron;
- (3) less than 20% of the pores in the microporous film have a pore size less than 0.014 micron;
- (4) less than 20% of the pores in the microporous film have a pore size greater than 0.13 micron ; and
- (5) the polymeric coating has a thickness such that the membrane
  - (i) has a  $P_{10}$  ratio, over at least one 10°C range between -5 and 15 °C, of at least 1.3;
  - (ii) has an oxygen permeability (OTR), at all temperatures between 20° and 25°C, of at least 775,000 ml/m<sup>2</sup>.atm.24 hrs (50,000 cc/100 inch<sup>2</sup>.atm.24 hrs; and
  - (iii) has a CO<sub>2</sub>/O<sub>2</sub> permeability ratio(R) of at least 1.5;

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the  $P_{10}$ , OTR and R values being measured at a pressure of  $0.035 \text{ kg/cm}^2$  (0.5 psi).

21. (New) A membrane according to claim 20 wherein at least 90% of the pores in the microporous film have a pore size less than 0.24 micron.

22. (New) A membrane according to claim 20 wherein substantially 100% of the pores in the microporous film have a pore size less than 0.24 micron.

23. (New) A membrane according to claim 20 wherein at least 80% of the pores in the microporous film have a pore size less than 0.15 micron and at least 70% of the pores in the microporous film have a pore size less than 0.11 micron.

24. (New) A membrane according to claim 20 which has an OTR at all temperatures between  $20^\circ\text{C}$  and  $25^\circ\text{C}$  of at least  $1,550,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $100,000 \text{ cc/inch}^2.\text{atm.24 hrs}$ ) and an R ratio of at least 2.5, the OTR and R values being measured at a pressure of  $0.035 \text{ kg/cm}^2$  (0.5 psi).

25. (New) A membrane according to claim 20 which has an OTR of at least  $2,325,000 \text{ ml/m}^2.\text{atm.24 hrs}$  ( $150,000 \text{ cc/100 inch}^2.\text{atm.24 hrs}$ ) measured at a pressure of  $0.07 \text{ kg/cm}^2$  (10 psi).

26. (New) A membrane according to claim 20 wherein the coating polymer is polydimethyl siloxane.

27. (New) A membrane according to claim 20 wherein the coating polymer is cis-polybutadiene, poly(4-methylpentene) or ethylene-propylene rubber.

28. (New) A membrane according to claim 20 wherein the coating polymer has been crosslinked.



29. (New) A package which is stored in air and which comprises
- (a) a sealed container, and
  - (b) within the sealed container, a respiring biological material and a packaging atmosphere around the biological material
- the sealed container including one or more permeable control sections which provide at least the principal pathway for oxygen and carbon dioxide to enter or leave the packaging atmosphere, at least one said permeable control section being a gas-permeable membrane as defined in claim 20.

### REMARKS

#### Amendments

#### In the specification.

The following comments are made on the numbered amendments to the specification.

1. The amendments to this paragraph note that this application is a continuation of Serial No. 08/759,602, and that the grandparent application Serial No. 08/453,108 has been abandoned.
2. The amendment to this paragraph is the insertion at the end of the paragraph, after "... the second heating cycle." on page 3, line 15 of the specification, of additional information about the conventional way in which the values of  $T_o$  and  $T_p$  are measured. The same amendment was made to the parent application.
3. The amendment to this paragraph is the replacement of the words "is now" on page 5, line 12, by the words -- was previously -- .

4. The amendment to this paragraph replaces the words "substantially the only pathways" on page 6, line 4, by the words -- at least the principal pathway, and optionally substantially the only pathway --. Basis for this amendment will be found on page 2, lines 22-25.

5. The amendment to this paragraph corrects and amplifies the information given about the preferred characteristics of the microporous film. The same amendment was made to the parent application. As noted in the parent application, basis for these amendments will be found in U.S. Patent No. 4,937,115, which is incorporated by reference in this and the parent application on page 8, lines 3-4. As the Examiner will see, the information inserted into the specification is disclosed at column 7, line 52, to column 8, line 12, of U.S. Patent No. 4,937,115. It should also be noted that there is an error (now corrected) on page 7, line 30, of the original specification, since the films in question are not made by methods which involve stretching. On the contrary, stretching should be avoided (see for example, column 2, line 53, and column 7, line 62, of U.S. Patent No. 4,937,115), because it results in pores of less uniform size. A copy of U.S. Patent No. 4,937,115 is attached.

6. The amendment to this paragraph is the deletion of the last sentence (" The  $\Delta H$  values... respectively."), on page 15, lines 21-22.

7. The amendment to this paragraph is the deletion of the last sentence (" The  $P_{10}$  ratios... increasing  $P_{10}$  ratios.") on page 18, lines 15-16.

8.-13. The amendments to the Tables, as set out above, are the insertion of asterisks before the numbers of the Examples which are comparative examples, because the membranes in question have oxygen permeabilities which are below the minimum specified in the revised claims.

14. and 15. The amendments to this paragraph and to Table 6, as set out above, are the correction of the units in which the temperatures are expressed from "°F" to -- °C --.

16. The amendment to this paragraph is the replacement of "in" by --, --, thus correcting a typographical error.

In the claims.

The amendments made to claims 1-19 as filed will be apparent from the attached Marked-up Version of the Amended Claims, and the content of the new claims 20-29 will be apparent from the new claims set out above. The following additional comments are made for the assistance of the Examiner.

General

The amended claims contained two independent claims, Claim 1 and claim 20. Amended Claim 1 requires that the microporous film was prepared by steps (A) - (I) as set out in the claim. New claim 20 requires not only that the microporous film has an average for size of less than 0.24 micron, but also that

at least 70% of pores have a pore size of less than 0.24 micron,  
less than 20% of the pores have a pore size less than 0.014 micron and  
less than 20% of pores have a pore size greater than 0.13 micron.

The requirements summarized above provide a sharp line of distinction over the Antoon reference (U.S. Patent No. 5, 160, 768) which was relied upon by the Examiner to reject the original claims in the parent application. Antoon discloses coated membranes comprising a specific type of microporous film and a coating thereon of a cured silicone elastomer. In the parent application, the claims were restricted to the use of crystalline polymers and the Examiner withdrew the rejection over Antoon. The independent claims in this continuation application, however, include membranes in which the coating on the microporous film is composed of a cured silicone elastomer.

The specific type of microporous film disclosed by Antoon is a uniaxially or biaxially oriented olefin (e.g. polypropylene or polyethylene) film containing 40-75% of a

filler (e.g. calcium carbonate). As noted in column 4, lines 48-59, of Antoon, the uniaxial or biaxial orientation of the filled olefin film causes the polymer to pull away from the filler, thus creating voids and pores in the film matrix. The random nature of the process used to manufacture Antoon's microporous films necessarily results in films having a wide range of pore sizes. In Applicants' invention, by contrast, the microporous film preferably has a relatively narrow range of pore sizes (see for example page 7, lines 29-30). This preferred feature of Applicants' invention has been made an essential feature of the amended claims of this continuation application, thus distinguishing them from Antoon. In amended Claim 1, this feature is incorporated by specifying that the microporous film was prepared by a process which inherently produces a narrow range of pore sizes (see page 7, line 29 - page 8, line 5, as amended). In new independent claim 20, this feature is incorporated directly, by narrowly defining the permissible percentages of pore sizes, both at the upper end and at the lower end of the range of sizes. Dependent claims 3-6 and 21-23 are limited to yet narrower classes of microporous film, further distinguishing from Antoon.

Basis for the amended claims 1-19 will be apparent from the attached Marked-up Version of Amended Claims and the following comments.

#### Claim 1

lines 1-2 "useful in the packaging of respiring biological materials"

page 14, lines 24-26

lines 3-4 "network of interconnected pores"

page 6, lines 18-20

lines 7-8 "average pore size less than 0.24 micron"

page 6, lines 20-21

lines 9-26 process for preparing the microporous film

page 7, line 29-page 8, line 5, as explained in detail above in connection with the amendment 5. to the specification.

Claims 3-5 at least 70%, or at least 90 %, or substantially 100%, of the pores have a pore size of less than 0.24 micron

page 6, lines 22-23

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- Claim 6 at least 80% of the pores have a pore size less than 0.15 micron and at least 70% have a pore size less than 0.11 micron  
page 6, lines 23-25
- Claim 7 OTR of at least 1,550, 000  
Claim 5
- Claim 16 at least the principal pathway  
page 2, lines 22-25

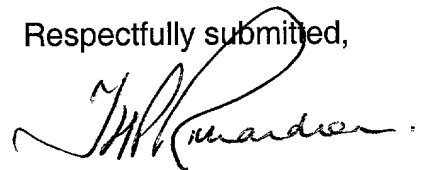
Basis for the new claims 20-29 will be apparent from the following comments.

- Claims 20-23 See Claim 1 and page 6, lines 20-29
- Claims 24-25 See amended claims 7 and 8
- Claims 26-28 See claims 11-13
- Claim 29 see amended Claim 16

### CONCLUSION

It is believed that this application is now in condition for allowance, and such action at an early date is earnestly requested. If, however, there are any outstanding issues, the Examiner is asked to call the undersigned in the hope that they can be resolved by a telephone interview.

Respectfully submitted,



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